Comparing Well-Defined Manganese, Iron, Cobalt, and Nickel Ketone Hydrosilylation Catalysts

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Received: 01.03.2014; Accepted after revision: 26.03.2014

Abstract: A brief review of manganese-catalyzed hydrosilylation is presented along with a personal account of how the design for the highly active catalyst, \([\eta^6-C_{10}H_8]Mn(CO)_3[BF_4]\), was conceived. The reductive transformations achieved using this catalyst are described and put into further context by comparing the observed activities with those attained for leading late first-row transition-metal catalysts.

Key words: catalysis, hydrosilylation, ketones, manganese, ligands

Due to the cost and relative toxicity associated with homogeneous precious metal catalysts, the search for sustainable alternatives that operate with competitive activities, selectivities, and lifetimes has continued to intensify. Much of this effort has centered around the development of late first-row transition-metal (Mn, Fe, Co, and Ni) catalysts, as these metals are earth-abundant and far less expensive than their precious metal counterparts.

While a wide range of organic transformations have been targeted, the development of first-row metal hydrosilylation catalysts remains of interest to the polysilane industry since platinum catalysts have long been used to prepare silicone coatings and elastomers. With this in mind, my colleagues and I recently reported the development of a well-defined manganese complex that is capable of mediating ketone hydrosilylation with turnover frequencies (TOF) of up to 76,800 h\(^{-1}\) at ambient temperature.

To put our discovery into perspective, a comparison of manganese-based hydrosilylation catalysts reported to date is essential. The initial mention of manganese-mediated hydrosilylation was published in 1983 by Pratt and Faltynek, more than 25 years after Speier and co-workers reported H\(_2\)PtCl\(_6\) to be an effective olefin hydrosilylation catalyst. The reductive transformation of ketone-containing substrates with TOF of up to 1,632 h\(^{-1}\) was achieved using \([\eta^6-C_{10}H_8]Mn(CO)_3\)[BF\(_4\)], which was found to exhibit improved, yet limited, TOF for ketone reduction of up to 99 h\(^{-1}\).

In 1999, Chung and co-workers reported the use of late first-row transition-metal acyl complexes to catalyze the hydrosilylation of ketone-containing substrates with TOF of up to 1,632 h\(^{-1}\). Moreover, this complex has been found to mediate the hydrosilylation of transition-metal acyl complexes.

Since these reports, manganese-based hydrosilylation chemistry has dealt exclusively with the reduction of carbonyl-containing substrates (Table 1). In 1995, the Cutler group reported \((\text{Ph}_2\text{PPrPDI})\text{Mn}\) to catalyze the hydrosilylation of ketones with moderate TOF of up to 350 h\(^{-1}\) at ambient temperature.

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Boxylic acids to yield disilylacetals or their related aldehydes; however, relatively modest TOF have been realized for both transformations. Chidara and Du have also reported that (3,5-t-Bu2-salen)MnN is capable of mediating the hydrosilylation of 4-nitrobenzaldehyde with a TOF of 11,760 h⁻¹; however, this transformation required heating to 80 °C. Further attempts to catalyze the hydrosilylation of benzaldehyde using 1 mol% of (3,5-t-Bu2-salen)MnN at room temperature have taken either 22 hours (in CDCl₃) or 47 hours (in C₆D₆) to reach completion.

When we first became interested in developing a manganese-based hydrosilylation catalyst, we hoped to design one that could operate with exceptional activities at mild temperatures. Considering the data in Table 1, along with the benzaldehyde hydrosilylation experiments reported for (3,5-t-Bu2-salen)MnN, it became clear that (PPh₃)(CO)₄MnC(O)Me remained the best-performing carbonyl hydrosilylation catalyst at ambient temperature. It has been found that a bulky κ₃-N,N,N-bis(imino)pyridine (or pyridine diimine, PDI) ligand could be used to mimic the coordination environment of mer-carboxyl ligands, allowing the preparation of an iron-based hydrogenation catalyst that operates efficiently under mild thermal conditions (Figure 1, a). With this in mind, we believed that a pentadentate PDI chelate could mimic the five neutral ligands of (PPh₃)(CO)₄MnC(O)Me and allow for the preparation of a manganese hydrosilylation catalyst with the general formula (κ₅-PDI)MnX, where X is an anionic ligand (Figure 1, b).

Furthermore, due to the redox noninnocent nature of PDI ligands, we recognized that it might be possible to improve upon (PPh₃)(CO)₄MnC(O)Me by designing a formally zerovalent manganese complex that had one or more electrons stored in the π-system of the ligand (Figure 2, a). This approach would obviate the need for a dedicated anionic ligand within the catalyst structure, while providing an open site for substrate binding. In order to prepare such a complex, the metalation of Ph₂PPrPDI with (THF)₂MnCl₂ was conducted, allowing the isolation of (Ph₂PPrPDI)MnCl₂. Reduction of this compound in the presence of excess Na/Hg (with or without 1,3,5,7-cyclooctatetraene present) enabled the preparation of (Ph₂PPrPDI)Mn (Figure 2, b). The characterization of this complex by X-ray diffraction, ¹H NMR and EPR spec-

### Table 1 Carbonyl Hydrosilylation Activities Reported for Well-Defined Manganese Catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>mol%</th>
<th>Temp (°C)</th>
<th>Substrate class</th>
<th>Product class</th>
<th>Silane used</th>
<th>Highest TOF (h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(PPh₃)(CO)₄MnC(O)Me</td>
<td>1.5–3.0</td>
<td>24</td>
<td>esters</td>
<td>ethers</td>
<td>PhSiH₃</td>
<td>22710</td>
</tr>
<tr>
<td></td>
<td>2.4</td>
<td>24</td>
<td>ketones</td>
<td>silyl ethers</td>
<td>PhMe₂SiH</td>
<td>1,63211</td>
</tr>
<tr>
<td>(η₃-C₆H₅)Mn(CO)₃</td>
<td>5.0</td>
<td>25</td>
<td>ketones</td>
<td>silyl ethers</td>
<td>Ph₃SiH</td>
<td>715</td>
</tr>
<tr>
<td>[(η₃-C₆H₅)Mn(CO)₃][BF₄]</td>
<td>0.5–5.0</td>
<td>25</td>
<td>ketones</td>
<td>silyl ethers</td>
<td>PhMe₂SiH</td>
<td>9916</td>
</tr>
<tr>
<td>Mn₂(CO)₁₀</td>
<td>1.0</td>
<td>100</td>
<td>amides</td>
<td>amines</td>
<td>Et₂SiH</td>
<td>617</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>25</td>
<td>carboxylic acids</td>
<td>disilylacetsalts</td>
<td>Et₂SiH</td>
<td>619</td>
</tr>
<tr>
<td>(3,5-t-Bu₂-salen)MnN</td>
<td>0.5</td>
<td>80</td>
<td>aldehydes</td>
<td>alcohols</td>
<td>PhSiH₃</td>
<td>11,76020</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>80</td>
<td>ketones</td>
<td>alcohols</td>
<td>PhSiH₃</td>
<td>58220</td>
</tr>
<tr>
<td>(Ph₂PPrPDI)Mn</td>
<td>0.01–1.0</td>
<td>25</td>
<td>ketones</td>
<td>silyl ethers</td>
<td>PhSiH₃</td>
<td>76,8007</td>
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<tr>
<td></td>
<td>1.0</td>
<td>25–80</td>
<td>esters</td>
<td>silyl ethers</td>
<td>PhSiH₃</td>
<td>187</td>
</tr>
</tbody>
</table>

**Figure 1** (a) Using a PDI ligand framework to mimic Fe(CO)₅. (b) Designing a Mn-based hydrosilylation catalyst with a κ₅-PDI ligand.

**Figure 2** (a) A PDI radical monoanion imitating the ligand field of (PPh₃)(CO)₄MnC(O)Me. (b) Electronic structure representation of (Ph₂PPrPDI)Mn.
troscopy revealed that (Ph₂PPrPDI)Mn likely consists of a low-spin, divalent manganese center that is coordinated to a singlet PDI dianion. However, the possibility that (Ph₂PPrPDI)Mn possesses a PDI radical monoanion that is antiferromagnetically coupled to an intermediate-spin manganese(I) center has yet to be ruled out computationally.

Having characterized (Ph₂PPrPDI)Mn, we set out to determine whether or not this complex is capable of mediating ketone hydrosilylation. Adding a 1:1 ratio of acetophenone and phenylsilane to 1 mol% of (Ph₂PPrPDI)Mn in benzene-d₆ solution resulted in complete ketone reduction after only four minutes at 25 °C. After comparing the activities observed for different silanes, we decided to continue our study with PhSiH₃, which enabled the fastest reaction times. We then sought to determine how the electronic and steric properties of the substrate would influence their relative ease of hydrosilylation. Several of the ketones investigated are shown in Scheme 1, along with the time needed to achieve >99% conversion at 25 °C.

As displayed in Scheme 1, varying the para position of acetophenone significantly extended the time it took for the reaction to reach completion, regardless of whether the substituent was electron donating or electron withdrawing in nature. Extended reaction times were also encountered when investigating the hydrosilylation of sterically demanding substrates such as dicyclohexyl ketone.

Realizing that the activity of (Ph₂PPrPDI)Mn appeared highly substrate dependent, efforts were made to scale up the hydrosilylation of readily reduced substrates to demonstrate the synthetic utility of our work. In the process, we also sought to enhance the desirability of this transformation by using lower catalyst loadings, eliminating the requirement for solvent, and by adding a substoichiometric amount of PhSiH₃ in order to improve atom-efficiency. These efforts are best summarized for the cyclohexanone reductions shown in Scheme 2. When the catalyst loading was lowered to 0.01 mol% in the absence of solvent, the hydrosilylation of cyclohexanone reached completion within five minutes (Scheme 2, a). Although the reagents were mixed at 25 °C, significant heat was generated due to the exothermic nature of the reaction. In turn, the isolated yield was a fairly low 64% due to evaporation of the reactants, equating to a TOF of 76,800 h⁻¹ (based on product recovery). When a 3:1 ratio of cyclohexanone to phenylsilane was added to 0.33 mol% of (Ph₂PPrPDI)Mn, complete utilization of the Si–H bonds was achieved within four hours to yield PhSi(OCy)₃, demonstrating that hydrosilylation could be conducted in an atom-efficient manner at ambient temperature (Scheme 2, b).

Finally, we investigated ester hydrosilylation using (Ph₂PPrPDI)Mn since (PPh₃)(CO)₄MnC(O)Me had been reported to catalyze ester deoxygenation to yield siloxane and the parent ether. Surprisingly, adding 1 mol% of (Ph₂PPrPDI)Mn to a benzene-d₆ solution containing a 1:1 ratio of MeOAc and PhSiH₃ resulted in the formation of four different quaternary silanes after 24 hours at 25 °C: PhSi(OMe)₂, PhSi(OMe)₂(OMe), PhSi(OEt)₂, and PhSi(OEt)₂(OMe). Repeating the experiment with PhSiD₃ confirmed that each ethoxide substituent was formed following reductive cleavage of the acyl C–O bond and carbonyl reduction. Although much longer reaction times (and/or heating to 80 °C) were required to achieve appreciable dihydrosilylation conversions for i-PrOAc, PhOAc, and t-BuOAc, the reduction of EtoAc into a 9:1 ratio of PhSi(OEt)₂ and PhSi(OEt)₂(OMe) had reached completion after 5.5 hours (Scheme 3). Although this reaction proceeded much slower (TOF = 18 h⁻¹) than the ester dihydrosilylation reactions reported by Cutler and coworkers (TOF up to 227 h⁻¹), it should be noted that (PPh₃)(CO)₄MnC(O)Me has not been found to catalyze the cleavage of ester acyl C–O bonds.
While the ambient temperature ester dihydrosilylation activities achieved for (P2P)PDI)Mn are relatively modest, this complex remains the most active manganese-based ketone hydrosilylation catalyst described to date (Table 1). Furthermore, the ketone hydrosilylation activities achieved for (P2P)PDI)Mn (TOF up to 76,800 h⁻¹) favorably compare to those reported for other late first-row metal hydrosilylation catalysts. Many iron-based precatalysts that mediate this transformation operate efficiently at 23 °C and those featuring the most impressive reported activities include [κ²-N-phosphinoamidate]Fe(N(SiMe₃)₂)₂ (TOF up to 23,600 h⁻¹),²⁶ Fe[N(SiMe₃)₂]₃ (TOF up to 2,400 h⁻¹),²⁷ (P2P)PDI)Fe(Ns)₂ (Ns = neosilyl; TOF up to 333 h⁻¹),²⁸ (Ppy)Box)Fe(Ns)₂ and (Ppy)Box)Fe(Ns)₂ (TOF up to 333 h⁻¹).²⁸ In contrast, cobalt-based carbonyl hydrosilylation catalysts have been achieved for with relatively poor TOF. For example, [Co(py)₃][BPh₄] remains the most active cobalt catalyst for ketone hydrosilylation at low temperatures (0–20 °C; TOF of 11 h⁻¹)³⁰ while attaining aldehyde hydrosilylation TOF of up to 50 h⁻¹ with a cobalt(III) hydride complex required heating to 40 °C. Nickel catalysts have achieved carbonyl hydrosilylation TOF of 225 h⁻¹ (for a PCP-supported nickel hydride complex)³² and 388 h⁻¹ [for (Cp)NiH(NHC)] at 23–25 °C; however, both catalysts are significantly more effective for aldehyde reduction than ketone reduction.

In summary, my colleagues and I have found that (P2P)PDI)Mn catalyzes the ambient-temperature hydrosilylation of carbonyl groups with activities that are ca. 3× higher than the most active iron catalyst,²⁶ >1500× higher than the most active cobalt catalysts,²⁶,³¹ and ca. 200× higher than the most active nickel catalyst reported to date.³³ We are currently working to determine the mechanism of this transformation while seeking to expand upon the range of substrates that can be effectively reduced. Additionally, we hope to determine how the redox noninnocence and pentadentate coordination of (P2P)PDI allows for efficient manganese-mediated ketone hydrosilylation so that these design characteristics can be applied to a number of first-row-metal-mediated transformations.³⁴

**Acknowledgment**

This work was supported as part of the Center for Bio-Inspired Solar Fuel Production, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award Number DE-SC0001016.

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Graphical Abstract

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